

6: Organic Chemistry I

6A. Introduction to Organic Chemistry

Basic definitions to know

Hydrocarbon is a compound consisting of hydrogen and carbon **only**

Saturated: Contain single carbon-carbon bonds only

Unsaturated : Contains a C=C double bond

Molecular formula: The formula which shows the actual **number of each type of atom**

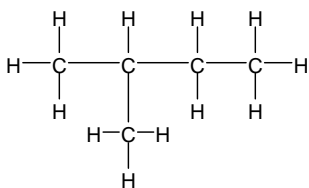
Empirical formula: shows the simplest whole number ratio of atoms of each element in the compound

General formula: algebraic formula for a homologous series e.g. C_nH_{2n}

Structural formula shows the minimal detail that shows the arrangement of atoms in a molecule, eg for butane: $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$,

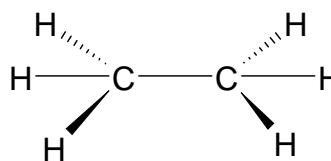
Displayed formula: show all the covalent bonds present in a molecule

Drawing Displayed formulae

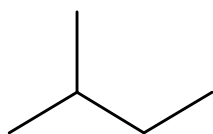


When drawing organic compounds add the hydrogen atoms so that each carbon has 4 bonds

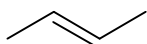
Remember that the shape around the carbon atom in saturated hydrocarbons is tetrahedral and the bond angle is 109.5°



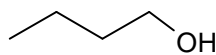
Skeletal formula shows the simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional Groups.



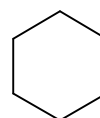
2-methylbutane



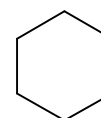
But-2-ene



Butan-1-ol



cyclohexane



cyclohexene

Homologous series are families of organic compounds with the **same functional group** and **same general formula**.

- They show a gradual change in physical properties (e.g. boiling point).
- Each member differs by CH_2 from the last.
- same chemical properties.

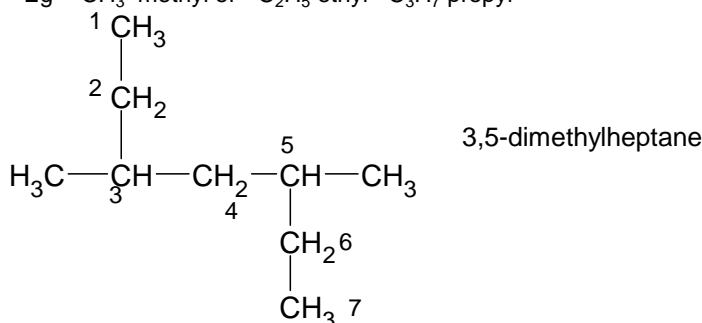
Functional group is an atom or group of atoms which when present in different molecules causes them to have similar chemical properties

homologous series	functional group	prefix / suffix (* = usual use)	example
Alkane		-ane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ Butane
Alkenes		suffix -ene	propene
Alcohols		suffix* -ol prefix hydroxy-	Propan-1-ol
Halogenoalkanes		prefix chloro- bromo- iodo-	1-chloropropane
Aldehydes		suffix -al prefix formyl-	ethanal
Ketones		suffix* -one prefix oxo-	Propanone
carboxylic acids		suffix -oic acid	Ethanoic acid
Esters		-yl -oate	methylethanoate

General rules for naming carbon chains

- Count the longest carbon chain and name appropriately
- Find any branched chains and count how many carbons they contain
- Add the appropriate prefix for each branch chain

Eg -CH₃ methyl or -C₂H₅ ethyl -C₃H₇ propyl



code	no of carbons
meth	1
eth	2
prop	3
but	4
pent	5
hex	6
hept	7
oct	8
non	9
dec	10

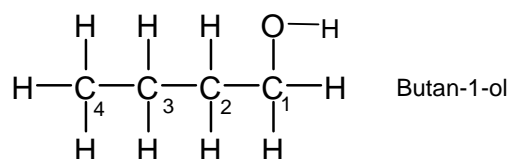
Basic rules for naming functional groups

- When using a suffix, add in the following way :

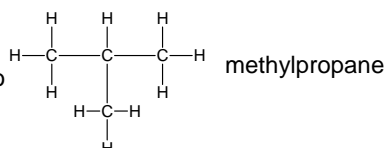
If the suffix starts with a vowel- remove the -e from the stem alkane name
e.g. Propan-1-ol, butan-1-amine, ethanoic acid, ethanoylchloride, butanamide

If the suffix starts with a consonant or there are two or more of a functional group meaning di, or tri needs to be used then **do not remove the -e** from the stem alkane name
e.g. Propanenitrile, ethane-1,2-diol, propanedioic acid, propane-1,2,3-triol, Pentane-2,4-dione.

- The position of the functional group on the carbon chain is given by a number – counting from the end of the molecule that gives the functional group the lowest number. For aldehydes, carboxylic acids & nitriles, the functional group is always on carbon 1.



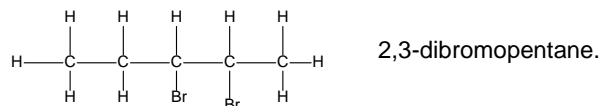
- We only include numbers, however, if they are needed to avoid ambiguity.



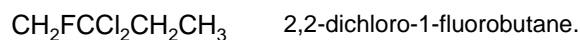
- The functional groups take precedence over branched chains in giving the lowest number

3-methylbut-1-ene is correct and not 2-methylbut-3-ene

- Where there are two or more of the same groups, *di-*, *tri-*, *tetra-*, *penta-* or *hexa-* are used. Note the point made above about the addition of 'e' to the stem



- Words are separated by numbers with dashes



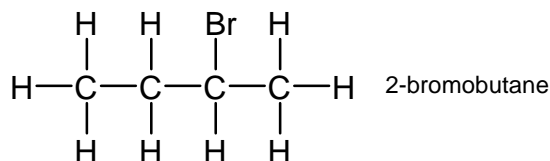
- numbers are separated by commas

- If there is more than one functional group or side chain, the groups are listed in alphabetical order (ignoring any *di*, *tri*).



Halogenoalkanes

Class the halogen as a substituent on the C chain and use the suffix **-fluoro**, **-chloro**, **-bromo**, or **-iodo**. (Give the position number if necessary)



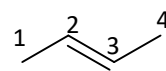
Alkenes

The double bond will be between two carbons. Use the lower number of the two to show the position of the double bond

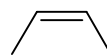
The name for alkenes may include E or Z at start to show the type of stereoisomer

If more than one double bond is present then suffix ends **diene** or **triene**. The stem ends in **a**

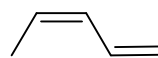
The suffix for alkenes can go in front of other suffixes.



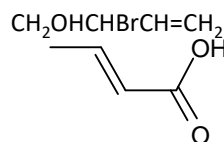
Double bond between C² and C³ so But-2-ene



Z-but-2-ene



Penta-1,3-diene



2-bromobut-3-en-1-ol

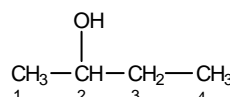
E-but-2-enoic acid

Alcohols

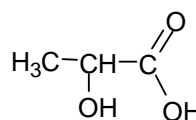
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

If the compound has an **-OH** group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix **hydroxy-**

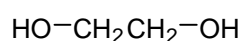
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



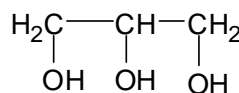
Butan-2-ol



2-hydroxypropanoic acid



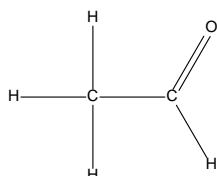
Ethane-1,2-diol



propane-1,2,3-triol

Aldehydes

An aldehyde's name ends in **-al**. It always has the C=O bond on the first carbon of the chain so it does not need an extra number. It is by default number one on the chain

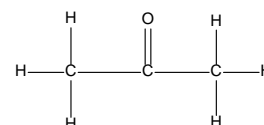


Ethanal

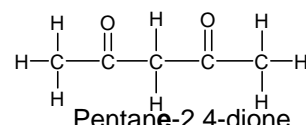
Ketones

Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one. If two ketone groups then **di** is put before **-one** and an **e** is added to the stem



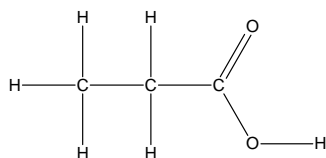
Propanone



Pentane-2,4-dione

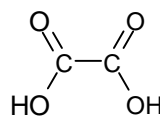
Carboxylic acids

These have the ending **-oic acid** but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end



Ethanoic acid

If there are carboxylic acid groups on both ends of the chain then it is called a **-dioic acid**



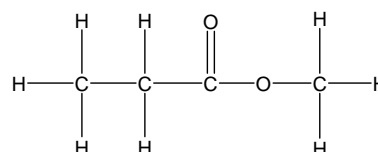
Ethanedioic acid

Note the **e** in this name

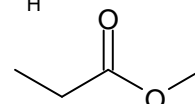
Esters

Esters have two parts to their names

The bit ending in **-yl** comes from the alcohol that has formed it and is next to the single bonded oxygen. The bit ending in **-anoate** comes from the carboxylic acid. (This is the chain including the C=O bond)



methylpropanoate



Isomers

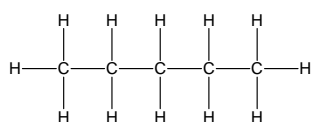
Structural isomers: same molecular formula different structures (or structural formulae)

Structural isomerism can arise from

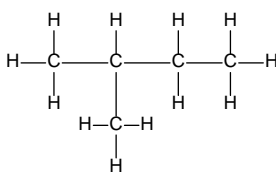
- Chain isomerism
- Position isomerism
- Functional group isomerism

EDEXCEL does not split structural isomers into the different categories. They are all classed as structural isomers.

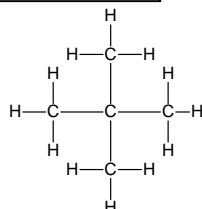
Chain isomers: Compounds with the same molecular formula but different structures of the carbon skeleton



pentane

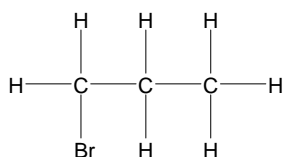


2-methylbutane

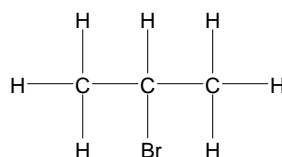


2,2-dimethylpropane

Position isomers: Compounds with the same molecular formula but different structures due to different positions of the same functional group on the same carbon skeleton

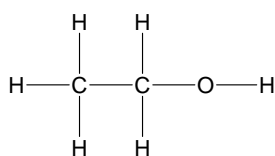


1-bromopropane

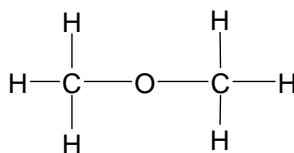


2-bromopropane

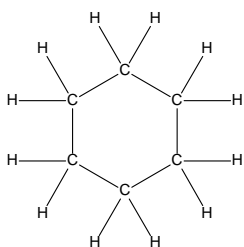
Functional group isomers: Compounds with the same molecular formula but with atoms arranged to give different functional groups



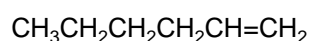
ethanol: an alcohol



Methoxymethane: an ether



Cyclohexane- cyclo alkane



hexene- alkene

Note: alkene and cyclo alkanes have the same general formula. Hexene and cyclohexane have the same molecular formula but have a different functional group

Stereoisomerism

Stereoisomers have the same structural formulae but have a different spatial arrangement of atoms.

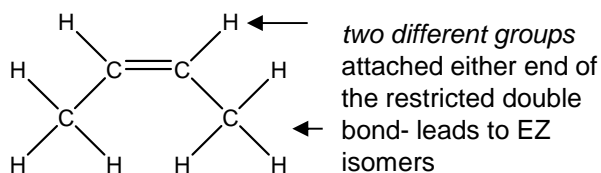
Alkenes can exhibit a type of isomerism called **E-Z stereoisomerism**

E-Z isomers exist due to restricted rotation about the C=C bond

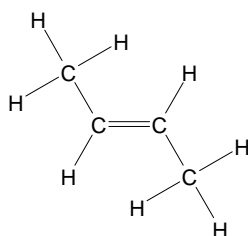
E-Z stereoisomers arise when:

- There is **restricted rotation** around the C=C double bond.
- There are **two different groups/atoms** attached both ends of the double bond

Single carbon-carbon covalent bonds can easily rotate

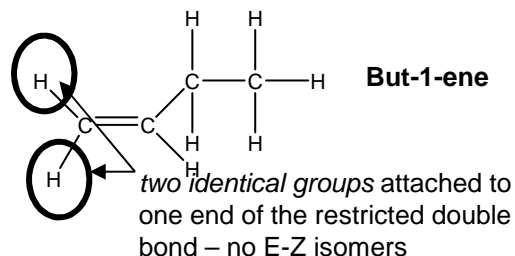


Z-but-2-ene



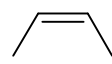
E-but-2-ene

These are two isomers as the lack of rotation around the double bonds means one cannot be switched to the other

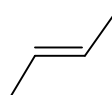


But-1-ene is a structural isomer of But-2-ene but does not show E-Z isomerism

Skeletal formulae can also represent E-Z isomerism



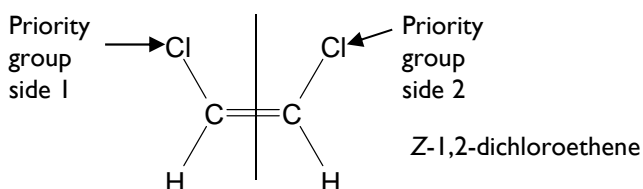
Z-but-2-ene



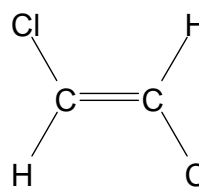
E-but-2-ene

Naming E-Z stereoisomers

First determine the priority groups on both sides of the double bond



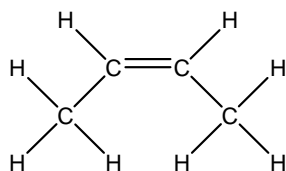
If the priority atom is on the same side of the double bond it is labelled Z from the german zusammen (The Zame Zide!)



E-1,2-dichloroethene

If the priority atom is on the opposite side of the double bond it is labelled E from the german entgegen (The Epposite side!)

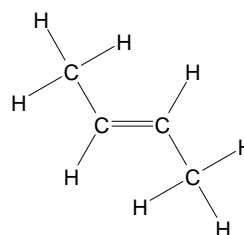
cis-trans isomerism is a special case of *EIZ* isomerism in which two of the substituent groups are the same.



Z-but-2-ene

Can also be called

Cis-but-2-ene



E-but-2-ene

Can also be called

trans-but-2-ene

6A Alkanes

Alkanes are saturated hydrocarbons

General formula alkane C_nH_{2n+2}

Saturated: Contain single carbon-carbon bonds only

Hydrocarbon is a compound consisting of hydrogen and carbon **only**

Fuels from crude oil

They are obtained from the crude oil in the order of fractional distillation, cracking and reformation of crude oil

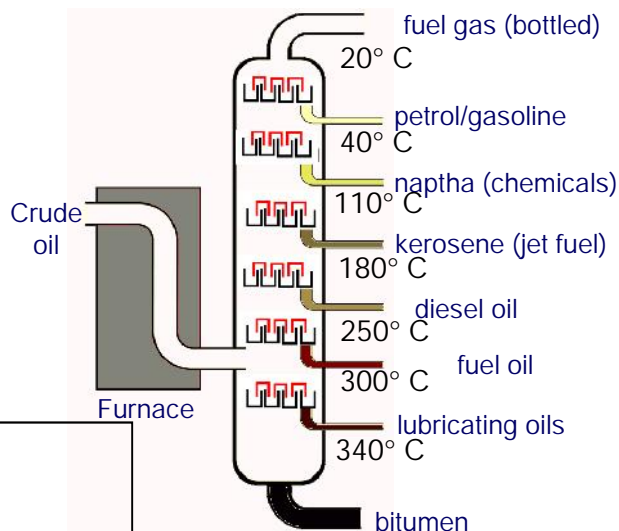
Alkanes are used as fuels

Refining crude oil

Fractional Distillation:

Petroleum is a mixture consisting mainly of alkane hydrocarbons

Petroleum fraction: mixture of hydrocarbons with a similar chain length and boiling point range



- Oil is pre-heated
- then passed into column.
- The fractions condense at different heights
- The temperature of column decreases upwards
- The separation depends on boiling point.
- Boiling point depends on size of molecules.
- The larger the molecule the larger the London forces
- Similar molecules (size, bp, mass) condense together
- Small molecules condense at the top at lower temperatures
- and big molecules condense at the bottom at higher temperatures.

This is a physical process involving the splitting of weak London forces between molecules

Cracking

Cracking: conversion of large hydrocarbons to smaller molecules by breakage of C-C bonds

High Mr alkanes \rightarrow smaller Mr alkanes + alkenes + (hydrogen)

Economic reasons for catalytic cracking

- The petroleum fractions with shorter C chains (e.g. petrol and naphtha) are in **more demand** than larger fractions.
- To make use of excess larger hydrocarbons and to supply demand for shorter ones, longer hydrocarbons are cracked.
- The products of cracking are **more useful and valuable** than the starting materials (e.g. ethene used to make poly(ethene) and ethane-1,2-diol, and ethanol) The smaller alkanes are used for motor fuels which burn more efficiently.

This is a chemical process involving the splitting of strong covalent bonds so requires high temperatures.

Reforming

Turns straight chain alkanes into branched and cyclic alkanes and Aromatic hydrocarbons

Branched and cyclic hydrocarbons burn more cleanly and are used to give fuels a higher octane number.

Used for making motor fuels

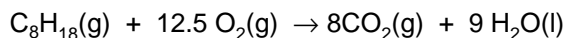
Alkanes as Fuels

Fuel : releases heat energy when burnt

Complete Combustion

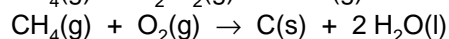
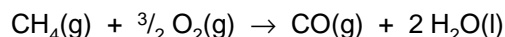
In excess oxygen alkanes will burn with complete combustion

The products of *complete* combustion are CO₂ and H₂O.



Incomplete Combustion

If there is a **limited amount of oxygen** then *incomplete* combustion occurs, producing CO (which is very toxic) and/or C (producing a sooty flame)



Alkanes readily burn in the presence of oxygen. This combustion of alkanes is highly exothermic, explaining their use as **fuels**.

Incomplete combustion produces less energy per mole than complete combustion.

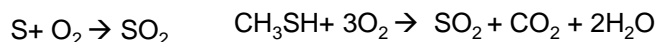
Carbon (soot)/particulates can cause global dimming- reflection of the sun's light

Carbon monoxide is an highly toxic but odourless gas. It can cause death if it builds up in a enclosed space due to faulty heating appliances.

CO is toxic to humans as CO can form a strong bond with haemoglobin in red blood cells. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin.

Pollution from Combustion

Sulphur containing impurities are found in petroleum fractions which produce SO₂ when they are burned.



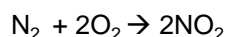
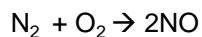
Coal is high in sulphur content, and large amounts of sulphur oxides are emitted from power stations.

SO₂ is acidic and will dissolve in atmospheric water and can produce **acid rain**.

Nitrogen Oxides NO_x

Nitrogen oxides form from the reaction between N₂ and O₂ inside the car engine.

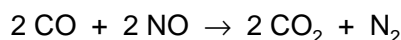
The **high temperature** and **spark** in the engine provides sufficient energy to break strong N₂ bond



Pollutant	Environmental consequence
Nitrogen oxides (formed when N ₂ in the air reacts at the high temperatures and spark in the engine)	NO is toxic and can form smog NO ₂ is toxic and acidic and forms acid rain
Carbon monoxide	toxic
Carbon dioxide	Contributes towards global warming
Unburnt hydrocarbons (not all fuel burns in the engine)	Contributes towards formation of smog
Soot/particulates	Global dimming and respiratory problems

Catalytic converters

These remove CO, NO_x and unburned hydrocarbons (e.g. octane, C₈H₁₈) from the exhaust gases, turning them into 'harmless' CO₂, N₂ and H₂O.



Converters have a ceramic honeycomb coated with a thin layer of catalyst metals
Platinum, Palladium, Rhodium
– to give a large surface area.

Biofuels

Most fossil fuels come from crude oil, which is a non-renewable resource. Fossil fuel reserves will eventually run out

Alternative fuels have been developed from renewable resources. Alcohols and biodiesel, which can both be made from plants, are two examples of renewable plant-based fuels

Alcohols such as ethanol can be produced from the fermentation of sugars from plants.

Biodiesel is produced by reacting vegetable oils with a mixture of alkali and methanol

Advantages of using Biofuels

Reduction of use of fossil fuels which are finite resources
biofuels are renewable

Use of biodiesel is more carbon-neutral

Allows fossil fuels to be used as a feedstock for organic compounds

No risk of large scale pollution from exploitation of fossil fuels

Disadvantages of Biofuels

Less food crops may be grown

Land not used to grow food crops

Rain forests have to be cut down to provide land

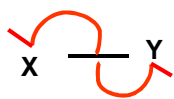
Shortage of fertile soils

Introduction to Mechanisms

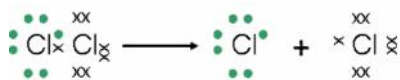
To understand how the reaction proceeds we must first understand how bonds are broken in organic mechanisms
There are two ways to break a covalent bond:

1. HOMOLYTIC FISSION:

each atom gets one electron from the covalent bond



one headed arrow shows movement of one electron



The bond has broken in a process called **homolytic** fission.

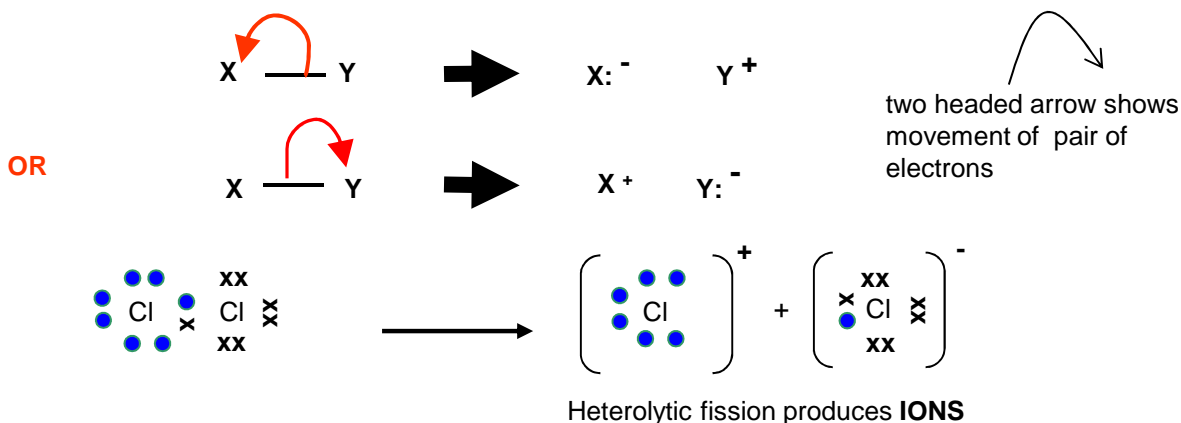
When a bond breaks by homolytic fission it forms two **Free Radicals**.

Free Radicals do not have a charge and are represented by a \cdot

DEFINITION

A **Free Radical** is a reactive species which possess an **unpaired electron**

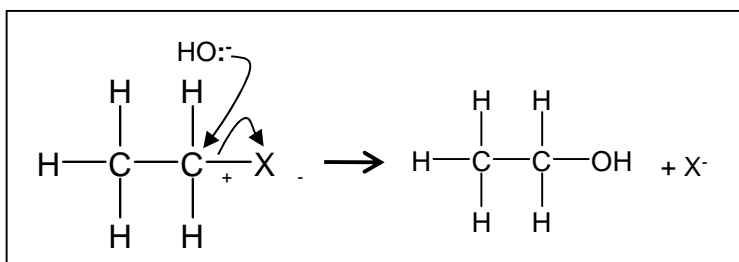
2. HETEROLYTIC FISSION: (*one atom gets both electrons*)



Most organic reactions occur via heterolytic fission, producing ions

The Mechanism:

To understand a reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism**



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen

We use curly arrows in mechanisms to show the movement of an electron pair showing either breaking or formation of a covalent bond;

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

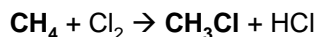
Free Radical Substitution Reactions of Alkanes

Reaction of alkanes with bromine / chlorine in UV light

In the presence of **UV light** alkanes react with chlorine to form a mixture of products with the halogens substituting hydrogen atoms.

In general, alkanes do not react with many reagents. This is because the C-C bond and the C-H bond are relatively strong.

Overall Reaction



methane chloromethane

This is the overall reaction, but a more complex mixture of products is actually formed

The **MECHANISM** for this reaction is called a **FREE RADICAL SUBSTITUTION**

It proceeds via a series of steps:

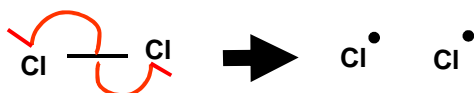
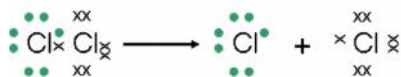
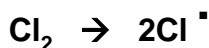
STEP ONE: **Initiation**

STEP TWO: **Propagation**

STEP THREE: **Termination**

STEP ONE Initiation

Essential condition: UV light



The UV light supplies the energy to break the Cl-Cl bond. It is broken in preference to the others as it is the weakest.

UV light does not have enough energy to break the C-H bond

The bond has broken in a process called **homolytic fission**.

*each atom gets **one** electron from the covalent bond*

When a bond breaks by homolytic fission it forms **Free Radicals**.

Free Radicals do not have a charge and are represented by a •

DEFINITION

A **Free Radical** is a reactive species which possess an **unpaired electron**

STEP TWO Propagation



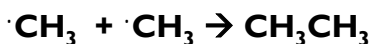
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a Cl₂ molecule to produce the main product and another Cl free radical

All propagation steps have a **free radical** in the **reactants** and in the **products**.

As the Cl free radical is regenerated, it can react with several more alkane molecules in a **CHAIN REACTION**

STEP THREE Termination



Collision of two free radicals *does not generate* further free radicals: the chain is **TERMINATED**.

Minor step leading to impurities of ethane in product. **Write this step using structural formulae** and don't use molecular formulae

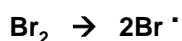
Applying the mechanism to other alkanes

Example: Write mechanism of Br₂ and Propane

The same mechanism is used: Learn the patterns in the mechanism

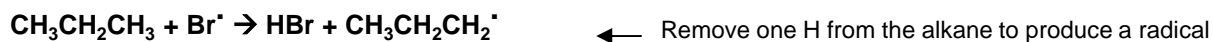
STEP ONE Initiation

Essential condition: UV light

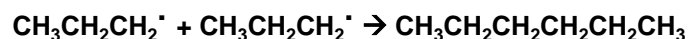


Br₂ splits in the same way as Cl₂

STEP TWO Propagation



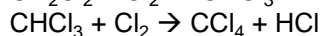
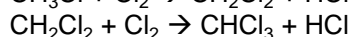
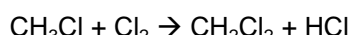
STEP THREE Termination



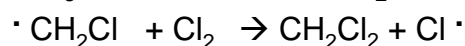
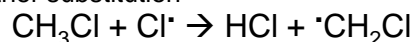
Further substitution

Excess Cl₂ present will promote further substitution and could produce **CH₂Cl₂, CHCl₃ and CCl₄**

These reactions could occur

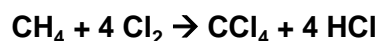


Example propagation steps that would lead to further substitution

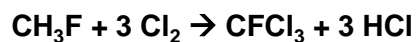


You should be able to write **overall reaction** equations for various reactions

Example 1. Write the overall reaction equation for the formation of CCl₄ from CH₄ + Cl₂



Example 2. Write the overall reaction equation for the formation of CFCI₃ from CH₃F + Cl₂



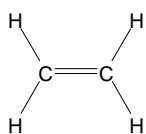
Note HCl is always the side product – never H₂

6C Alkenes

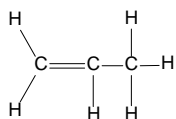
Alkenes are unsaturated hydrocarbons

General formula is C_nH_{2n}

Alkenes contain a carbon-carbon double bond somewhere in their structure

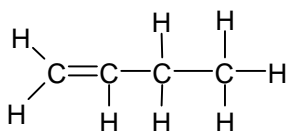


Ethene

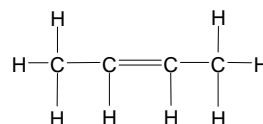


Propene

Numbers need to be added to the name when positional isomers can occur

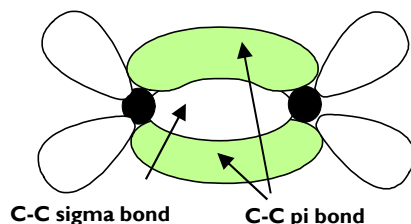


But-1-ene



But-2-ene

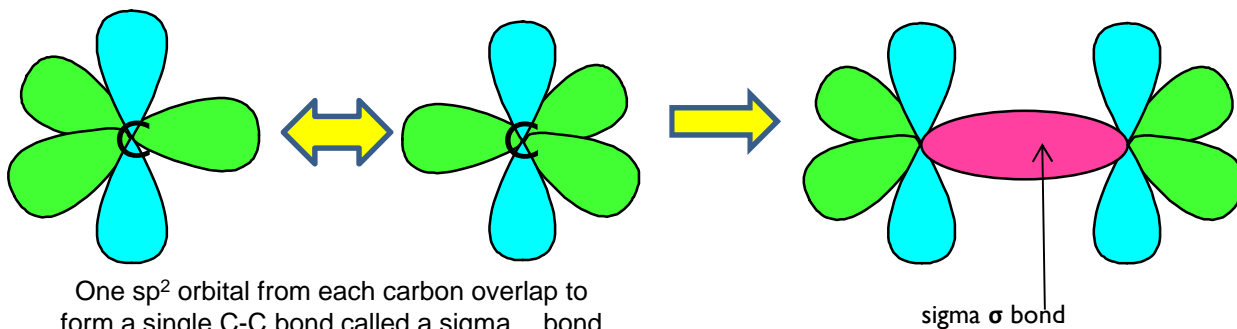
$C=C$ double covalent bond consists of **one sigma (σ) bond and one pi (π) bond.**



bonds are **exposed** and have **high electron density**.

They are therefore vulnerable to attack by species which 'like' electrons: these species are called **electrophiles**.

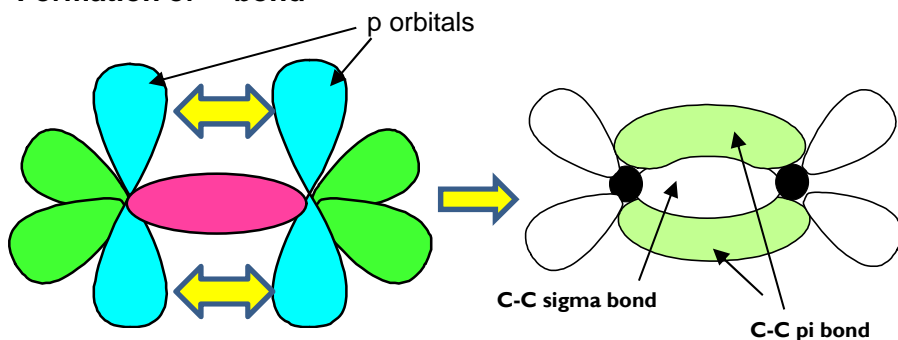
Formation of σ bond



One sp^2 orbital from each carbon overlap to form a single C-C bond called a sigma bond

Rotation can occur around a sigma bond

Formation of π bond



The π bond is formed by sideways overlap of two p orbitals on each carbon atom forming a π -bond above and below the plane of molecule.

The π bond is weaker than the σ bond.

There is Restricted rotation about a π bond

The π bond leads to resultant high electron density above and below the line between the two nuclei

Addition Reactions of Alkenes

Addition reaction: a reaction where two molecules react together to produce one

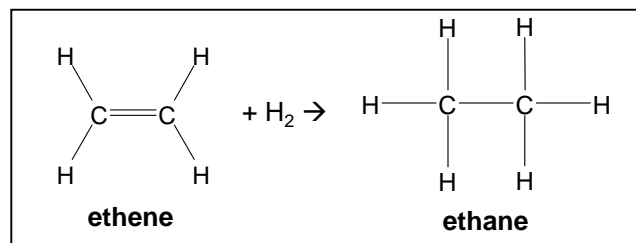
1. Reaction of Alkenes with Hydrogen

Change in functional group: alkene → alkane

Reagent: hydrogen

Conditions: Nickel Catalyst

Type of reaction: Addition/Reduction



Electrophilic Addition: Reactions of Alkenes

A π bond is weaker than a σ bond so less energy is needed to break π bond
The π bonds in alkenes are areas with high electron density. This is more accessible to electrophilic attack by electrophiles. Alkenes undergo addition reactions.

Definition Electrophile: an electron pair acceptor

2. Reaction of Alkenes with bromine/chlorine

Change in functional group:

alkene → dihalogenoalkane

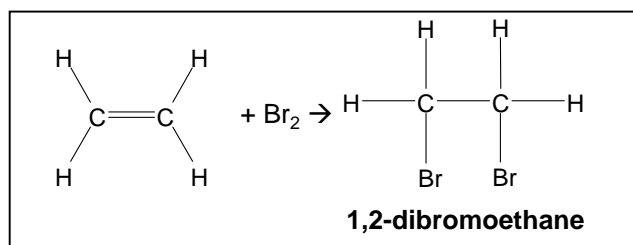
Reagent: Bromine (dissolved in organic solvent)

Conditions: Room temperature (not in UV light)

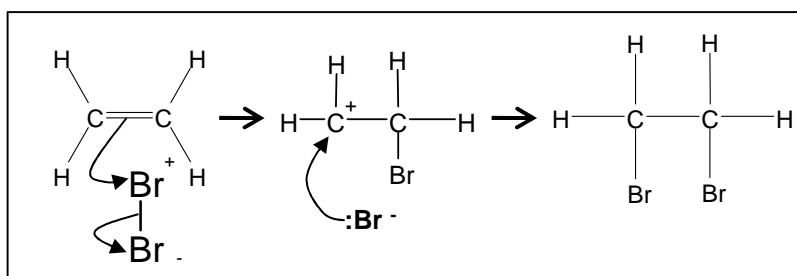
Mechanism: Electrophilic Addition

Type of reagent: Electrophile, Br δ^+

Type of Bond Fission: Heterolytic



As the Br₂ molecule approaches the alkene, the pi bond electrons repel the electron pair in the Br-Br bond. This **INDUCES** a **DIPOLE**. Br₂ becomes **polar** and **ELECTROPHILIC** (Br δ^+).



The **INTERMEDIATE** formed, which has a positive charge on a carbon atom is called a **CARBICATION**

3. Reaction of Hydrogen Bromide with alkenes

Change in functional group:

alkene → halogenoalkane

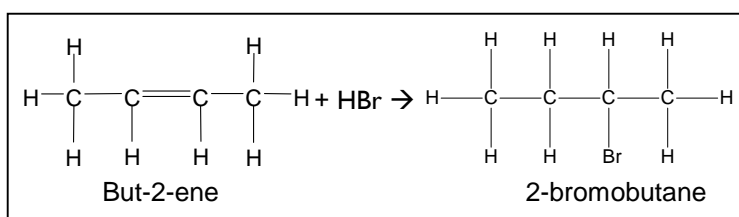
Reagent: HCl or HBr

Conditions: Room temperature

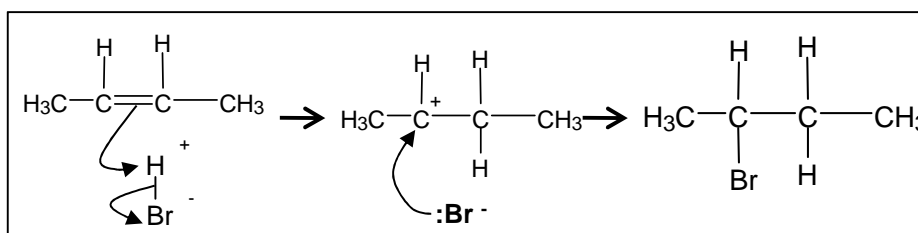
Mechanism: Electrophilic Addition

Type of reagent: Electrophile, H δ^+

Type of Bond Fission: Heterolytic

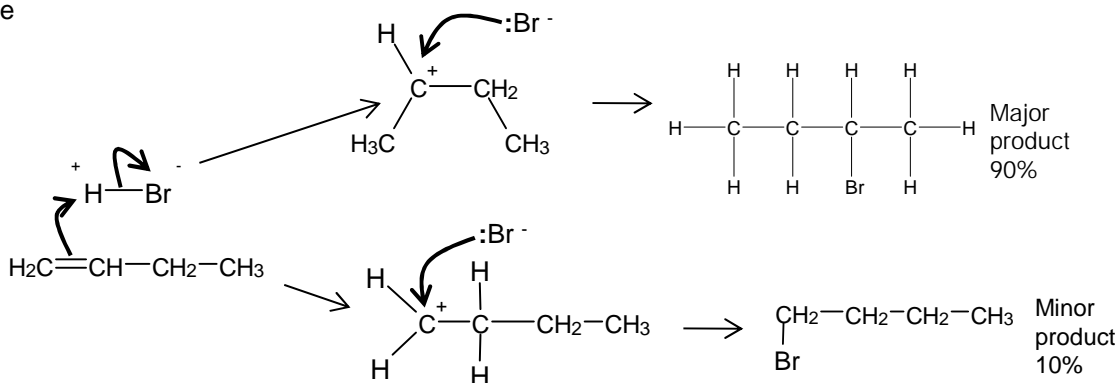


HBr is a polar molecule because Br is more electronegative than H. The H δ^+ is attracted to the electron-rich pi bond.



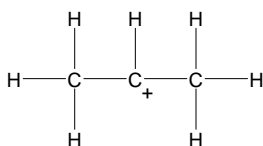
If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products.

But-1-ene will form a mixture of 1-bromobutane and 2-bromobutane on reaction with hydrogen bromide



WHY?

This carbocation intermediate is more stable because the methyl groups on either side of the positive carbon are electron releasing and reduce the charge on the ion which stabilises it.



The order of stability for carbocations is tertiary > secondary > primary

In **electrophilic addition** to alkenes, the **major product** is formed **via the more stable carbocation** intermediate.

In exam answers

- Draw out both carbocations and identify as primary, secondary and tertiary
- State which is the more stable carbocation e.g. secondary more stable than primary
- State that the more stable carbocation is stabilised because the methyl groups on either (or one) side of the positive carbon are electron releasing and reduce the charge on the ion.
- (If both carbocations are secondary then both will be equally stable and a 50/50 split will be achieved)

4. Reaction of Potassium Manganate(VII) with Alkenes

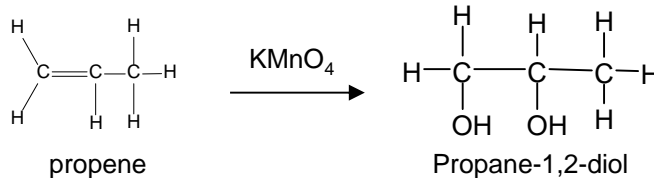
Change in functional group: alkene → diol

Reagent: KMnO_4 in an acidified solution

Conditions: Room temperature

Type of reaction: Oxidation

Observation: purple colour of MnO_4^- ion will decolourise to colourless



This reaction with its colour change can be used as a test for the alkene functional group. It would not change colour with alkanes

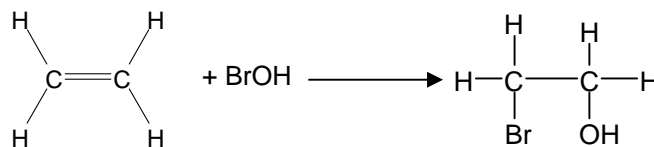
5. Reaction of Bromine Water with Alkenes

Reagent: Bromine dissolved in water

Conditions: Room temperature

Type of reaction: Addition

Observation: Orange colour of bromine water will decolourise to colourless

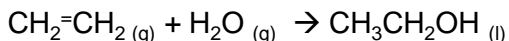


This reaction with its colour change is used as a test for the alkene functional group.

hydration of alkenes to form alcohols

Industrially alkenes are converted to alcohols in one step rather than the two in the above sulphuric acid reaction. They are reacted with water in the presence of an acid catalyst.

This reaction can be called **hydration**: a reaction where water is **added** to a molecule



Essential Conditions

High temperature 300 to 600°C

High pressure 70 atm

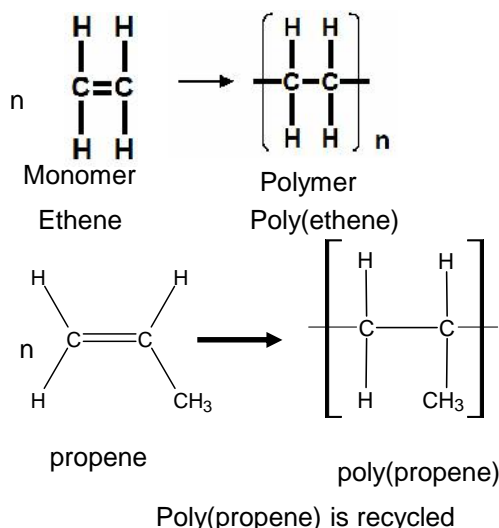
Catalyst of **concentrated H₃PO₄**

The high pressures needed mean this cannot be done in the laboratory. It is preferred industrially, however, as there are no waste products and so has a high atom economy. It would also mean separation of products is easier (and cheaper) to carry out. See equilibrium chapter for more on the industrial conditions for this reaction.

Addition Polymers

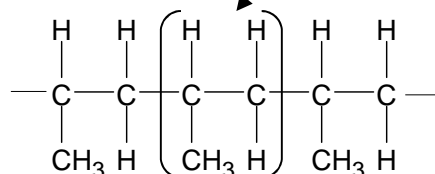
Addition polymers are formed from alkenes

This is called **addition polymerisation**



Poly(alkenes) like alkanes are unreactive due to the strong C-C and C-H bonds.

be able to recognise the repeating unit in a poly(alkene)



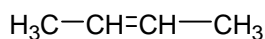
← Add the **n**'s if writing an equation showing the reaction where 'n' monomers become 'n' repeating units

Poly(ethene): is used to make plastics bags, buckets, bottles. It is a flexible, easily moulded, waterproof, chemical proof, and low density plastic.

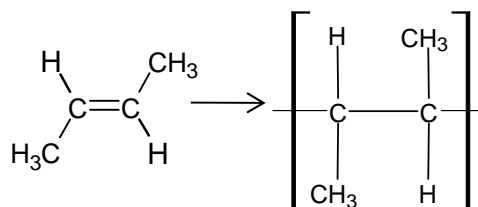
Poly(propene) is a stiffer polymer, used in utensils and containers and fibres in rope and carpets.

You should be able to draw the polymer repeating unit for any alkene

e.g. For but-2-ene



It is best to first draw out the monomer with groups of atoms arranged around the double bond



Methods of disposal of waste Polymers

Incineration

Rubbish is burnt and energy produced is used to generate electricity.

Some toxins can be released on incineration. (e.g. Combustion of halogenated plastics (ie PVC) can lead to the formation of toxic, acidic waste products such as HCl.) Modern incinerators can burn more efficiently and most toxins and pollutants can be removed. Greenhouse gases will still be emitted though.

Volume of rubbish is greatly reduced.

Recycling

Saves raw materials- nearly all polymers are formed from compounds sourced/produced from crude oil. Saves precious resources.

Polymers need collecting/ sorting- expensive process in terms of energy and manpower.

Polymers can only be recycled into the same type – so careful separation needs to be done.

Thermoplastic polymers can be melted down and reshaped.

feedstock for cracking

Polymers can be cracked into small molecules which can be used to make other chemicals and new polymers- Saves raw materials-

Chemists have designed ways to remove toxic waste products like HCl before they are emitted into the atmosphere. The waste gases from the incinerator are scrubbed/reacted with a base or carbonate. The base reacts with the acidic HCl gas, neutralising it (eg $\text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O}$)

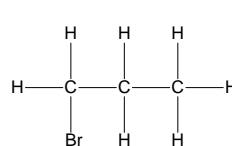
Chemists have also develop biodegradable and compostable polymers. Biodegradable polymers can be made from substances such as maize and starch

6D Halogenoalkanes

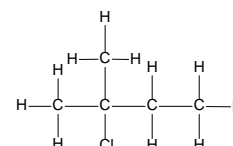
Naming Halogenoalkanes

Based on original alkane, with a *prefix* indicating halogen atom:
Fluoro for F; Chloro for Cl; Bromo for Br; Iodo for I.

Substituents are listed **alphabetically**



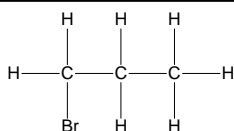
1-bromopropane



2-chloro-2-methylbutane

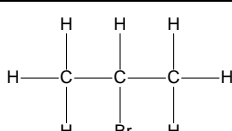
Classifying Halogenoalkanes

Halogenoalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.



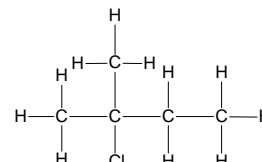
Primary halogenoalkane

One carbon attached to the carbon atom adjoining the halogen



Secondary halogenoalkane

Two carbons attached to the carbon atom adjoining the halogen



Tertiary halogenoalkane

Three carbons attached to the carbon atom adjoining the halogen

Reactions of Halogenoalkanes

Halogenoalkanes undergo either **substitution** or **elimination** reactions

Nucleophilic substitution reactions

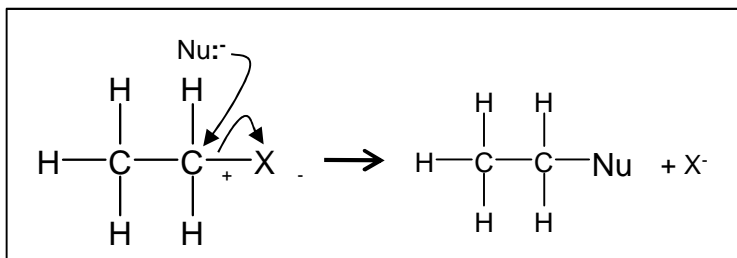
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donator e.g. :OH^- , :NH_3 , CN^-

The Mechanism: We draw (or **outline**) mechanisms to show in detail how a reaction proceeds

:Nu represents any nucleophile – they always have a **lone pair** and act as **electron pair donors**

The nucleophiles attack the positive carbon atom



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen



We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

The rate of these substitution reactions depends on the strength of the C-X bond

The weaker the bond, the easier it is to break and the faster the reaction.

The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

	Bond enthalpy / kJmol^{-1}
C-I	238
C-Br	276
C-Cl	338
C-F	484

Comparing the rate of hydrolysis reactions

Hydrolysis is defined as the splitting of a molecule (in this case a halogenoalkane) by a reaction with water



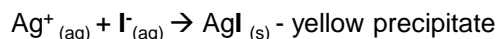
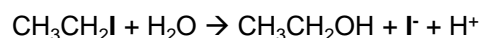
Aqueous silver nitrate is added to a halogenoalkane and the halide leaving group combines with a silver ion to form a **SILVER HALIDE PRECIPITATE**.

The precipitate only forms when the halide ion has left the halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

The **quicker** the **precipitate** is formed, the **faster** the **substitution** reaction and the **more reactive** the haloalkane

The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

Water is a **poor nucleophile** but it can react **slowly** with halogenoalkanes in a substitution reaction



The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest

$\text{AgI}_{(\text{s})}$ - yellow precipitate
 $\text{AgBr}_{(\text{s})}$ - cream precipitate
 $\text{AgCl}_{(\text{s})}$ - white precipitate

↑ forms faster

Nucleophilic substitution with aqueous hydroxide ions

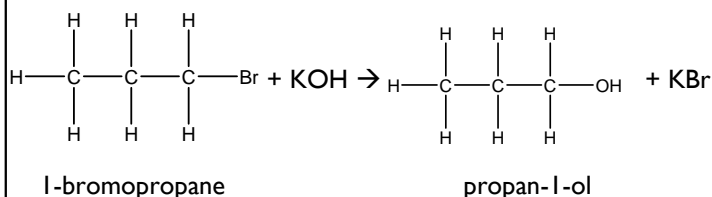
Change in functional group: halogenoalkane → alcohol

Reagent: potassium (or sodium) hydroxide

Conditions: In **aqueous solution**; Heat under reflux

Mechanism: Nucleophilic Substitution

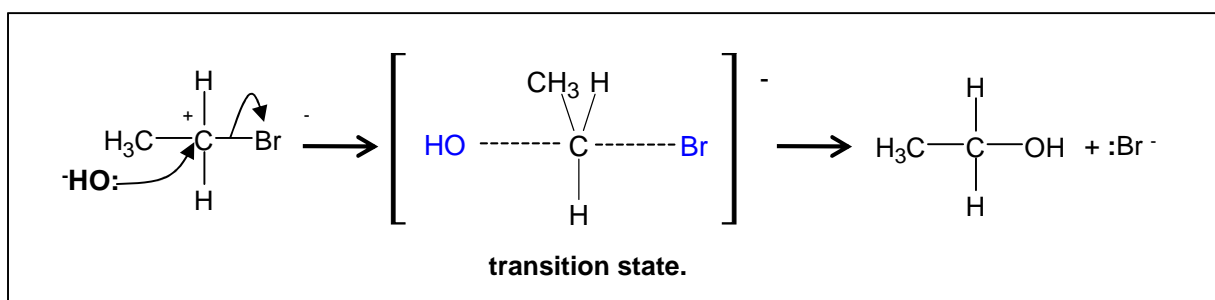
Role of reagent: Nucleophile, OH^-



The OH^- is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the C^+

The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs

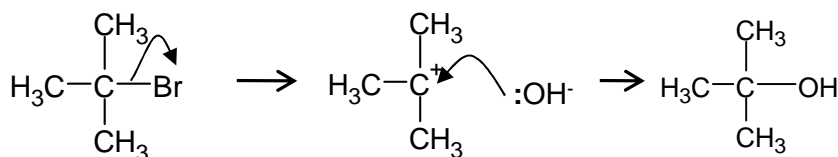
$\text{S}_{\text{N}}2$ nucleophilic substitution mechanism for halogenoalkanes



This mechanism occurs with primary halogenoalkanes

SN₁ nucleophilic substitution mechanism for tertiary halogenoalkanes

Tertiary haloalkanes undergo nucleophilic substitution in a different way



The Br first breaks away from the haloalkane to form a carbocation intermediate

The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is made stabilised by the electron releasing methyl groups around it. (see alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above

Primary halogenoalkanes don't do the SN₁ mechanism because they would only form an unstable primary carbocation.

Nucleophilic substitution with ammonia

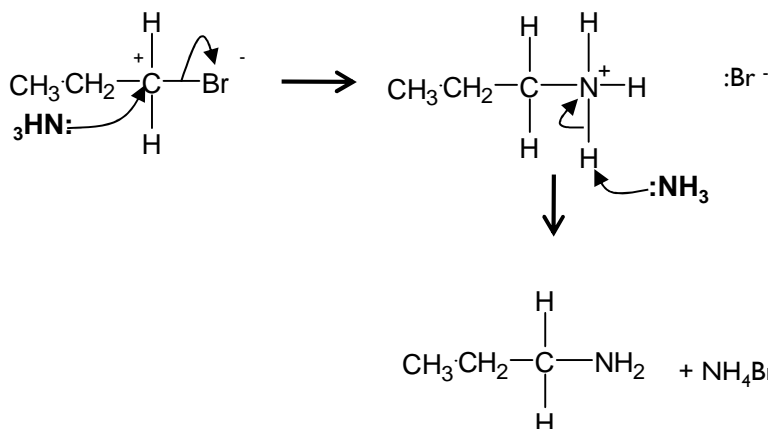
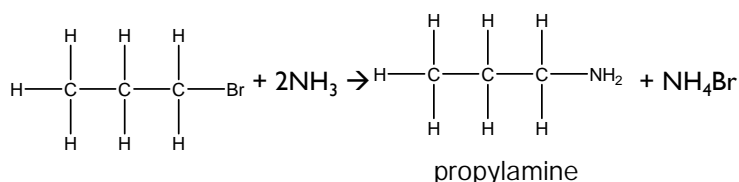
Change in functional group: halogenoalkane → amine

Reagent: NH₃ dissolved in ethanol

Conditions: Heating under pressure in a sealed tube

Mechanism: Nucleophilic Substitution

Type of reagent: Nucleophile, :NH₃



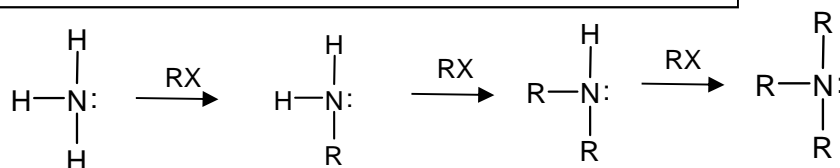
Naming amines:

In the above example propylamine, the propyl shows the 3 C's of the carbon chain.

Sometimes it is easier to use the IUPAC naming for amines e.g. Propan-1-amine

Further substitution reactions can occur between the haloalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.

Further reactions



Elimination reaction of halogenoalkanes

Elimination: removal of small molecule (often water) from the organic molecule

Elimination with alcoholic hydroxide ions

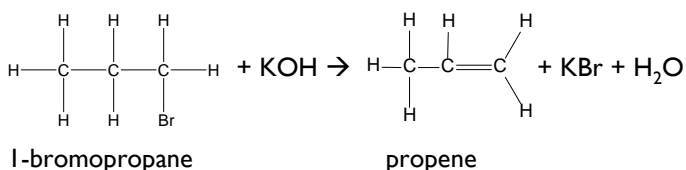
Change in functional group: halogenoalkane → alkene

Reagents: Potassium (or sodium) hydroxide

Conditions: In *ethanol*; Heat

Mechanism: Elimination

Role of reagent: Base, OH⁻



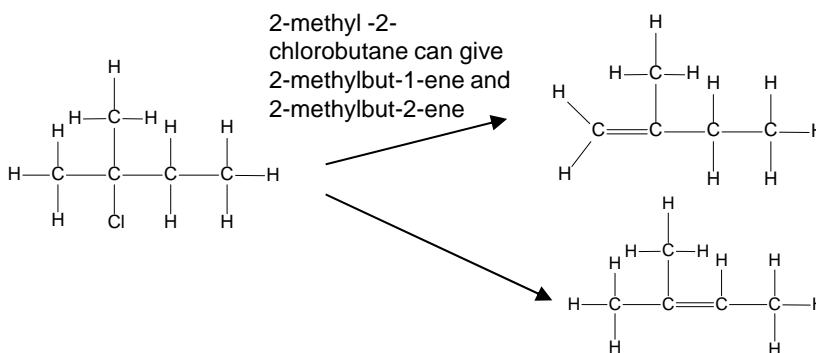
Note the importance of the solvent to the type of reaction here.

Aqueous: substitution

Alcoholic: elimination

Often a mixture of products from both elimination and substitution occurs

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed



The structure of the halogenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.

Primary tends towards substitution

Tertiary tends towards elimination

Uses of halogenoalkanes

Haloalkanes have been used as **refrigerants**, **fire retardants**, pesticides and **aerosol propellants**

chloroalkanes and chlorofluoroalkanes can be used as solvents

CH₂Cl₂ was used as the solvent in dry cleaning

Some halogenoalkanes have low flammability

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the ozone layer

6E Alcohols

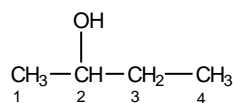
General formula alcohols $C_nH_{2n+1}OH$

Naming Alcohols

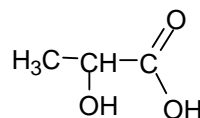
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

If the compound has an **-OH** group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix **hydroxy-**:

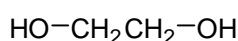
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



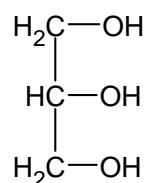
Butan-2-ol



2-hydroxypropanoic acid



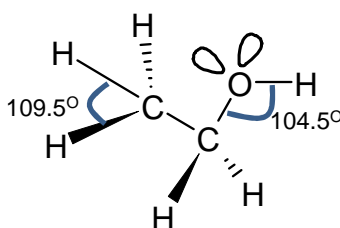
Ethane-1,2-diol



propane-1,2,3-triol

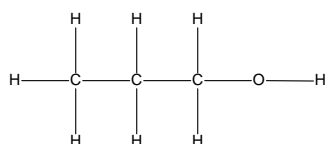
Bond angles in Alcohols

All the H-C-H bonds and C-C-O are 109.5° (tetrahedral shape), because there are 4 bond pairs of electrons repelling to a position of minimum repulsion.



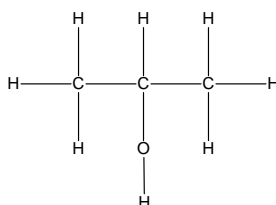
The H-O-C bond is 104.5° (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

Different types of alcohols



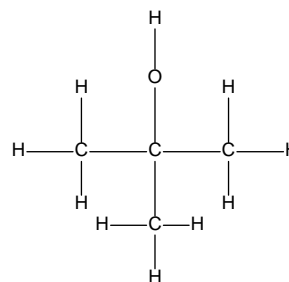
Propan-1-ol
Primary

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen



Propan-2-ol
Secondary

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen

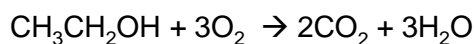


methylpropan-2-ol
Tertiary

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen

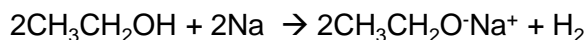
1. Combustion of Alcohols

Alcohols combust with a clean flame



2. Reaction of Alcohols with Sodium

Sodium reacts with alcohols



This reaction can be used as a test for alcohols

Observations:

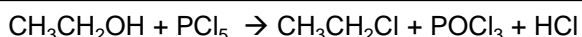
- effervescence,
- the mixture gets hot,
- sodium dissolves,
- a white solid is produced.

3. Substitution reactions of Alcohols to form Halogenoalkanes

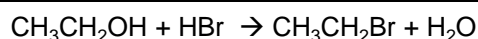
Various halogenating compounds can be used to substitute the -OH group for a halogen

PCl_5 / PCl_3 / conc HCl / SOCl_2 / mixture of NaCl + H_2SO_4 can all be used for substituting a Cl

Reaction with phosphorous (V) halide

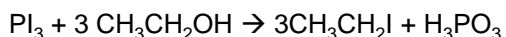


This reaction with PCl_5 (phosphorous(v)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.



For Br use KBr, 50% concentrated H_2SO_4 to produce HBr

Reaction with phosphorous (III) iodide



The **phosphorous (III) iodide** is produced in situ by reacting red phosphorus and iodine.

The reaction of KI and conc H_2SO_4 can't be used to produce HI because the sulphuric acid will oxidise the hydrogen halides to other products

4. Oxidation reactions of the alcohols

Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ is an oxidising agent that causes alcohols to oxidise.

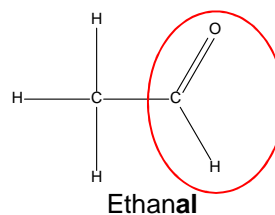
The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

Partial Oxidation of Primary Alcohols

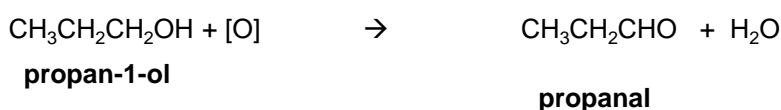
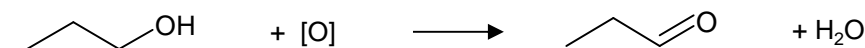
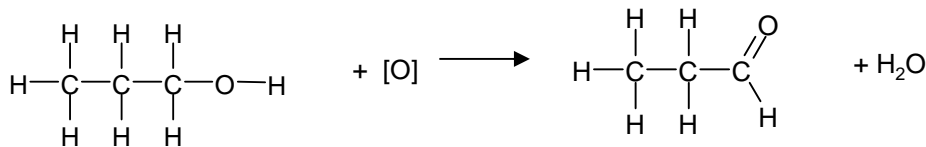
Reaction: primary alcohol \rightarrow aldehyde

Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.

Conditions: (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:



An aldehyde's name ends in **-al**
It always has the C=O bond on the first carbon of the chain so it does not need an extra number



Observation: the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) reduces to the green Cr^{3+} ion

Write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent

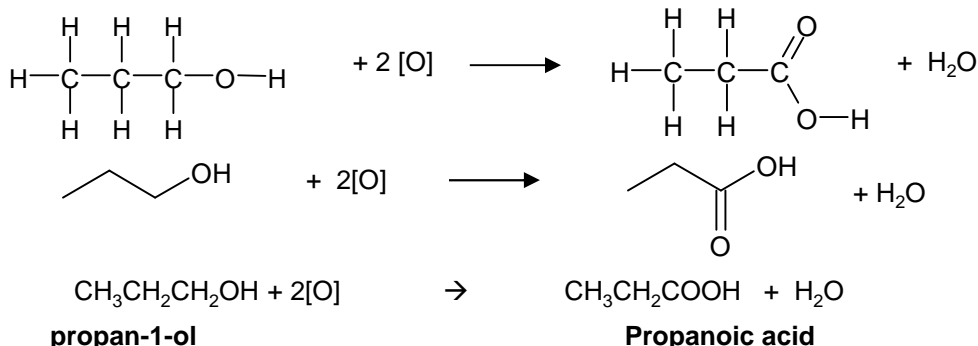
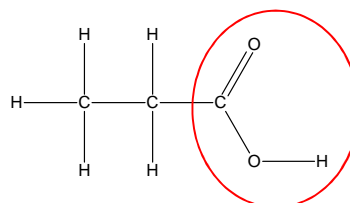
When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g. $\text{CH}_3\text{CH}_2\text{CHO}$

Full Oxidation of Primary Alcohols

Reaction: primary alcohol → carboxylic acid

Reagent: potassium dichromate(VI) solution and dilute sulphuric acid

Conditions: use an excess of dichromate, and **heat under reflux**: (distill off product after the reaction has finished)



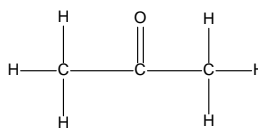
Observation: the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) reduces to the green Cr^{3+} ion

Oxidation of Secondary Alcohols

Reaction: secondary alcohol → ketone

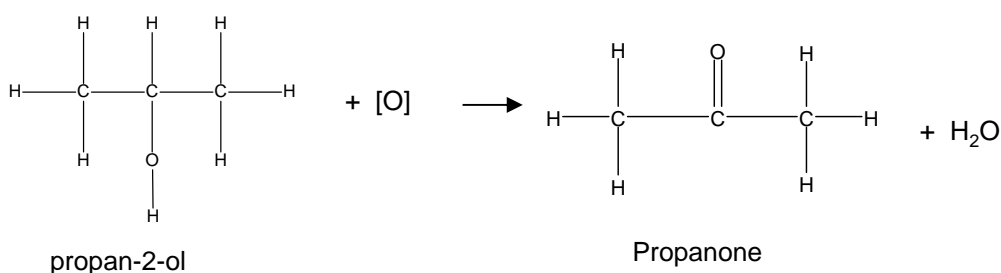
Reagent: potassium dichromate(VI) solution and dilute sulphuric acid.

Conditions: heat under reflux



Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one



Observation: the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) reduces to the green Cr^{3+} ion

There is no further oxidation of the ketone under these conditions.

Tertiary alcohols cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the OH group

Distinguishing between Aldehydes and Ketones

The fact that aldehydes can be further oxidised to carboxylic acids whereas ketones cannot be further oxidised is the chemical basis for tests that are commonly used to distinguish between aldehydes and ketones

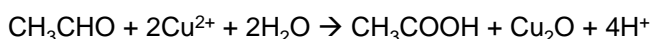
Fehling's (Benedict's) solution

Reagent: Fehling's Solution containing blue Cu^{2+} ions.

Conditions: heat gently

Reaction: **aldehydes only** are oxidised by Fehling's solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide

Observation: **Aldehydes**: Blue Cu^{2+} ions in solution change to a red precipitate of Cu_2O . **Ketones do not react**



The presence of a carboxylic acid can be tested by addition of sodium carbonate. It will fizz and produce carbon dioxide

Reaction of Alcohols with Dehydrating Agents

Reaction: Alcohol \rightarrow Alkene

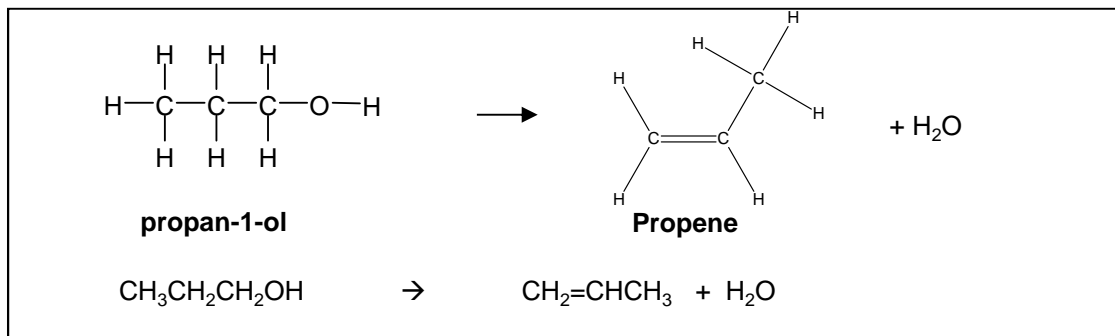
Reagents: Concentrated Phosphoric acid

Conditions: warm (under reflux)

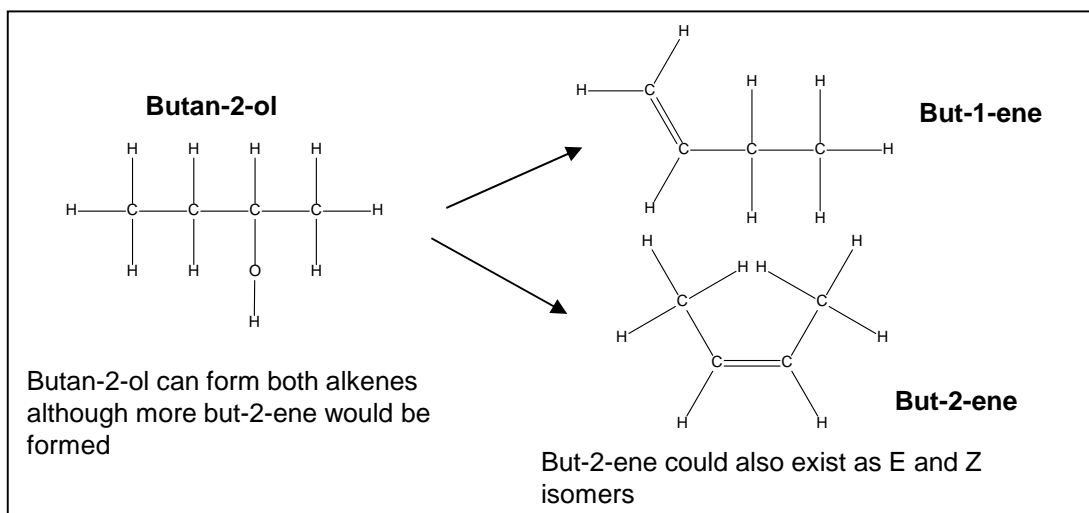
Role of reagent: dehydrating agent/catalyst

Type of reaction: acid catalysed elimination

Dehydration Reaction: removal of a water molecule from a molecule



Some 2° and 3° alcohols can give more than one product, when the double bond forms between different carbon atoms



Producing alkenes from alcohols provides a possible route to polymers without using monomers derived from oil

Organic techniques

Distillation

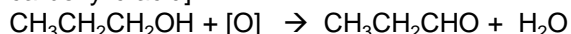
In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

Classic AS reaction using distillation

Reaction: primary alcohol \rightarrow aldehyde

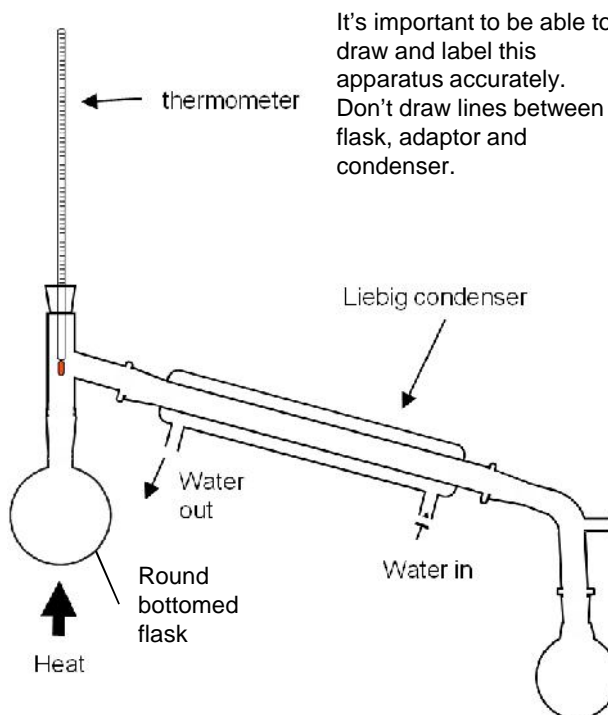
Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.

Conditions: use a limited amount of dichromate and **warm gently and distil** out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]



Observation

Orange dichromate solution changes to green colour of Cr^{3+} ions



It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser.

Reflux

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

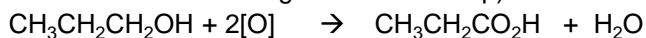
Never seal the end of the condenser as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated

Classic AS reaction using reflux

Reaction: primary alcohol \rightarrow carboxylic acid

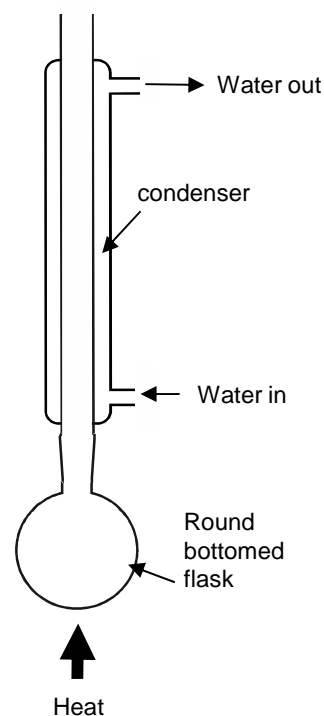
Reagent: potassium dichromate(VI) solution and dilute sulphuric acid

Conditions: use an excess of dichromate, and **heat under reflux**: (distill off product after the reaction has finished using distillation set up)



Observation

Orange dichromate solution changes to green colour of Cr^{3+} ions



Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles

It's important to be able to draw and label this apparatus accurately.

- Don't draw lines between flask and condenser.
- Don't have top of condenser sealed
- Condenser must have outer tube for water that is sealed at top and bottom
- Condenser must have two openings for water in and out that are open

Electric heaters are often used to heat organic chemicals. This is because organic chemicals are normally highly flammable and could set on fire with a naked flame.

Purifying an organic liquid

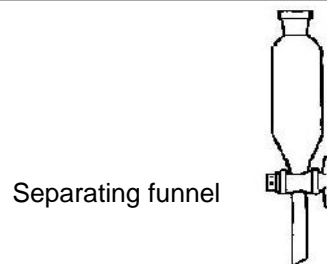
- Put the distillate of impure product into a separating funnel
- wash product by adding either
 - sodium hydrogencarbonate solution, shaking and releasing the pressure from CO_2 produced.
 - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (anhydrous sodium sulphate) to dry the organic liquid.
- Carefully decant the liquid into the distillation flask
- Distill to collect pure product

Sodium hydrogencarbonate will neutralise any remaining reactant acid.

Sodium chloride will help separate the organic layer from the aqueous layer

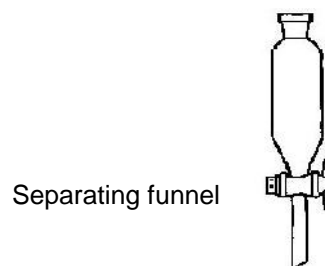
The drying agent should

- be insoluble in the organic liquid
- not react with the organic liquid



Solvent extraction

Mix organic solvent and oil-water mixture in a separating funnel then separate the oil layer.
Distil to separate oil from organic solvent
Add anhydrous CaCl_2 to clove oil to dry oil
Decant to remove CaCl_2



Measuring boiling point

Purity of liquid can be determined by measuring a boiling point. This can be done in a distillation set up or by simply boiling a tube of the sample in an heating oil bath.

Pressure should be noted as changing pressure can change the boiling point of a liquid

Measuring boiling point is not the most accurate method of identifying a substance as several substances may have the same boiling point.

To get a correct measure of boiling point the thermometer should be above the level of the surface of the boiling liquid and be measuring the temperature of the saturated vapour.